SURFACE AND INTERFACIAL FT-IR SPECTROSCOPIC STUDIES OF LATTICES

Kevin W. Evanson and Marek W. Urban
Department of Polymers and Coatings
North Dakota State University, Fargo, ND 58105

INTRODUCTION

Although polymer lattices and their technology have been established many years ago, an extensive effort is given to develop novel modes of preparation of lattices, techniques for cleaning and methods for determining their surface or bulk characteristics. While monodispersity and the particle size diameter are essential factors determining film properties, it is also important to establish the role of surfactants and the effects of external factors which govern their distribution in the latex films.

Recently, Zhao et al. have demonstrated the kinetics of surfactant exudation in latex films containing anionic surfactants by ATR FT-IR. Surfactant enrichment at both the film-air and film-substrate interface was observed. The enrichment was dependant upon the nature of the surfactant, the interface involved, the global concentration of surfactant and the coalescence time. However, analysis of surfactant exudation in the early stages of coalescence as well as the effects of the substrate and mechanical elongation have not been reported.

The present study is concerned with a SDOSS/EA/MAA (sodium dioctyl sulfo-succinate/ethyl acrylate/methacrylic acid) latex system in which the polarity of the system was modified by the addition of a small fraction of acid monomer. In most lattices a small percentage of acid monomer is incorporated to improve adhesion, increase stability of the latex particles, control viscosity and provide crosslinking sites for interparticle thermosetting reactions. ATR, Circle ATR, and photoacoustic FT-IR techniques are employed to the analysis of latex films at the film-substrate and film-air interfaces.

EXPERIMENTAL

Ethyl acrylate and methacrylic acid monomers were copolymerized by a semicontinuous emulsion polymerization process in a glass four neck break-away reaction vessel under a nitrogen purge. A typical recipe included: DDI water, 53.4%; ethyl acrylate, 42.1%; methacrylic acid, 1.9%; sodium dioctyl sulfo-succinate (SDOSS, Aerosol OT; American Cyanamid), 2.0%; and ammonium persulfate, 0.26%. The preparation of the pure copolymer was carried out using a procedure reported earlier. All films were prepared to maintain the film thickness between 75 and 100 μm. Upon deposition, the films were air dried for 72 hours (unless otherwise specified) at 23°C. The glass transition temperature of the latex films (-5°C) was determined from the average of three runs on a DuPont Instruments 910 differential scanning calorimeter equipped with a DuPont Thermal Analyzer 2000. The temperature range was from -50 to 250°C at a heating rate of 20°C/min. Attenuated total reflectance (ATR), Circle ATR, and photoacoustic (PA) FT-IR techniques were used to analyze latex films and the spectral conditions were reported earlier.

RESULTS AND DISCUSSION

Before we begin the analysis of the surface infrared spectra of ethyl acrylate-methacrylic acid copolymer latex, let us set the stage by defining the relevant features in the infrared spectra of all individual components of the latex. Figure 1 illustrates photoacoustic FT-IR spectra of sodium
diocetyl sulfo-succinate (trace A), ethyl acrylate/methacrylic acid copolymer only (trace B), and the corresponding ethyl acrylate-methacrylic acid copolymer latex (trace C). While all three spectra exhibit a strong carbonyl band due to alkyl ester groups centered at 1735 cm\(^{-1}\), the shoulder at 1703 cm\(^{-1}\) appears only in the spectra of the solution copolymer acrylate (trace B) and the latex (trace C). The 1703 cm\(^{-1}\) shoulder is characteristic of carboxylic acid dimers which have a tendency to form strong intermolecular hydrogen bonding. The presence of SO\(_2\) groups in the surfactant is manifested by the strong band at 1050 cm\(^{-1}\) (trace A), attributed to the symmetric S-O stretching vibrations of the sodium sulfonate groups. A closer examination of the latex spectrum (trace C) indicates however the presence of two bands at 1056 and 1046 cm\(^{-1}\).

In an effort to establish if the exudation of surfactant occurs, the latex film infrared spectra at the film-air and film-substrate interface were recorded using Circle ATR FT-IR spectroscopy. Figure 2 illustrates a series of ATR FT-IR spectra recorded at the film-air (trace A) and film-substrate (trace B) interfaces. Similarly to the PA FT-IR results, the spectra of the film-air interface indicates the presence of the bands at 1056 and 1046 cm\(^{-1}\). Changing the configuration of the sample with respect to the Circle ATR crystal allows us to detect the film-substrate interface. Trace B of Figure 2 illustrates the results of this analysis. The absence of both the 1056 and 1046 cm\(^{-1}\) bands indicates that surfactant is displaced from the film-air interface during coalescence. Taking advantage of the high water solubility of the surfactant, the film-air interface was washed with DBI water-MeOH (80:20 v/v). Such a surface modified sample was analyzed at the film-air interface and the resulting spectra is shown in Figure 2, trace C. It is apparent that the bands at 1056 and 1046 cm\(^{-1}\) are absent, such as that seen in trace B. These observations indicate a greater concentration of surfactant at the film-air interface.

Since exudation of the surfactant away from the film-substrate interface occurs during the latex film formation, the process can be monitored using Circle ATR. Figure 3 illustrates infrared spectra recorded as a function of time. Trace A exhibits a shoulder at 1046 cm\(^{-1}\) assigned to the S-O asymmetric stretching mode of hydrated SO\(_2\) groups. As the film formation proceeds, the 1046 cm\(^{-1}\) band diminishes as illustrated by traces A (5 min.), B (30 min.), and C (4 hours). After 4 hours, the film is completely transparent, and the band at 1046 cm\(^{-1}\) is no longer present. While the concentration gradient of the surfactant across the latex film has been reported earlier, it is apparent that during the early stages only one band at 1046 cm\(^{-1}\) is detected, whereas the film-air interface exhibits an additional band at 1056 cm\(^{-1}\). The origin of the 1046 and 1056 cm\(^{-1}\) bands will be presented in the near future.

Recently, Vanderhoff reported that surfactants may become insoluble in the polymer film and are then forced to the film-air interface due to incompatibility. Moreover, as a result of surface tension and surface tension differentials, surfactants may accumulate at the colloid interface in order to lower the high surface tension present between the polymer and the air. Such water soluble surfactants may be carried to the film-air interface during coalescence by the water flux that passes between latex particles during film formation. As the water diffuses out of the film and away from the substrate, one would expect to see the bands due to surfactant diminish. Additionally, the spectra collected at the film-air interface for the case where a second layer of latex was prepared over a pre-existing latex film resulted in very pronounced increases of the bands due to surfactant, indicating that the excess surfactant may diffuse with the water flux through the film. The transient intensity changes of the 1046 cm\(^{-1}\) band are associated with and parallel the disappearance of a broad band around 3400 cm\(^{-1}\) attributed to water evaporating from the film.
During the course of this study it was noted that both the surface energy of the substrate and mechanical stretching of the latex film may affect the intensity of the bands at 1056 and 1046 cm\(^{-1}\). Therefore, it is appropriate to address the question as to the effect of the surface tension at the substrate and the effect of film removal on the surfactant distribution. In an effort to gain further knowledge about these factors, we have used a rectangular ATR cell as the most convenient means of analysis. Figure 4, trace A, illustrates the film-air interface spectrum, whereas trace B is the film-substrate interface obtained for a 75 μm film cast on a PTFE (polytetrafluoroethylene). Similarly to the Circle ATR measurements, the spectrum of the film-air interface shows the presence of two bands at 1056 and 1046 cm\(^{-1}\). Surprisingly, however, the spectrum of the film-substrate interface (trace B), reveals the presence of the bands at 1056 and 1046 cm\(^{-1}\), not present in the spectrum recorded by Circle ATR. The only difference between the two measurements is that in order to obtain the film-substrate spectrum, the sample must be removed from the PTFE substrate. Thus, it was our hypothesis that the presence of surfactant at the film-substrate interface in the rectangular ATR mode of detection may be influenced by the increased surface tension brought on by mechanical stretching of the film during film removal from the substrate.

In order to verify this hypothesis, the latex films were prepared in the same manner as before. The excess of surfactant was removed from the film-substrate and the film-air interfaces by washing it with a MeOH/H\(_2\)O solution after which the films were allowed to air dry. Next, the films were elongated (20%) in a manner that closely approximated that encountered during the initial removal from the substrate. Figure 5 illustrates the spectral changes occurring at the film-substrate interface recorded as a function of time. The initial spectrum (trace A), does not exhibit the bands at 1056 and 1046 cm\(^{-1}\). However, after elongation (traces B-E), the presence of the 1056 and 1046 cm\(^{-1}\) bands becomes more pronounced with time. These results indicate that elongation of the film influences the distribution of surfactant throughout the latex film. By stretching the film, the surface area of the latex is increased, which results in a lower concentration of surfactant at the surface. In order to lower this increased surface tension, more surfactant at the interface is required and therefore diffuses to this interface.

While elongation experiments reveal the nature of surfactant exudation upon stretching, at this point we will address the issue of the effect of substrate surface tension on the surfactant distribution across the latex films. For that reason the latex films were prepared on liquid mercury. This enables the speedy removal of the films from the substrate with minimal mechanical disturbance to the film. Furthermore, it provides additional information as to the effect of the substrate surface tension (Hg, 416 mN/m; 20°C) along with the ability of monitoring the film-substrate and the film-air interfaces. Figure 6 illustrates spectra in the region from 1130 to 970 cm\(^{-1}\) obtained for the films coalesced on a layer of Hg. Traces A and B represent the film-substrate and the film-air interfaces, respectively, while trace C is the spectrum of the latex copolymer free of surfactant. It appears that the intense 1046 cm\(^{-1}\) band is much stronger at the film-substrate interface which is manifested by comparison with the 1025 cm\(^{-1}\) band. Although these results demonstrate the complexity of the surfactant distribution throughout latex films, it is apparent that the exudation of surfactant is a function of the water flux out of the film as well as the surface tension.

Using a simplistic view, it is known that a liquid will wet a solid surface of higher surface energy. The films prepared on the PTFE substrate with a low surface tension (18.5 mN/m)
exhibit an excess of surfactant at the film-substrate interface. Since most polymeric materials have surface tension in the range of 25-60 mN/m, they do not wet the PTFE surface. In order to lower the interfacial surface tension difference, the surfactant diffuses to the film-substrate interface. In the case of the films prepared on liquid mercury, the initial interface boundary is between two liquids. Due to the high surface tension of mercury, the mercury is wetted by the latex. However, as coalescence proceeds and water leaves the system, a solid polymeric film is formed which now acts as the substrate with a much lower surface energy compared to the mercury. Therefore, surfactant diffuses to this interface in order to lower the interfacial surface tension difference. In contrast, the Circle ATIR result indicates a greater extent of surfactant on the latex film surface and no detectable amount of surfactant at the film-substrate interface. This is attributed to the lower surface tension of the polymer with respect to the ATR crystal (appr. 70 mN/m) which is able to wet the glass surface. Therefore, there is no driving force to maintain the water soluble surfactant at the interface and it thus diffuses away with the water flux out of the film.

CONCLUSIONS
During the initial stages of coalescence, water evaporates from the film. As a result, the surfactant, as being incompatible with the copolymer, is carried out of the film by the water flux. As the film coalesces, an excess of surfactant is detected at the film-air interface. However, the direction of surfactant exudation will change when there is a large surface energy difference between the substrate and the latex film. This process is governed by interfacial surface tension differentials and is clearly observed in the case of films prepared on mercury where a higher concentration of surfactant at the film-substrate interface is found. The elongation studies reveal that the surfactant within the continuous phase may be forced to exudate to the lower interface by mechanical extension of the latex films. Finally, these studies demonstrate the utility of FT-IR spectroscopy for the analysis of the film-air and the film-substrate interfaces along with the distribution of surfactant throughout the latex films.

REFERENCES
Figure 1. PA FT-IR spectra: A) SDSOS (surfactant only); B) EA/MAA copolymer; C) EA/MAA latex.

Figure 2. Circle ATR FT-IR spectra of EA/MAA latex: A) Film-air interface; B) Film-substrate interface; C) Film-air interface washed with MeOH/H2O.

Figure 3. Circle ATR FT-IR spectra of EA/MAA latex collected as a function of time: A) 5 min.; B) 30 min.; C) 4 hrs.

Figure 4. ATR FT-IR spectra of EA/MAA latex prepared on PTFE: A) Film-air interface; B) Film-substrate interface.

Figure 5. ATR FT-IR spectra of EA/MAA latex prepared on PTFE, washed with MeOH/H2O and elongated 20%: A) No elongation; B) 0.15 hrs.; C) 0.5 hrs.; D) 0.75 hrs.; E) 1.25 hrs.

Figure 6. ATR FT-IR spectra of EA/MAA latex prepared on liq. mercury: A) Film-substrate interface; B) Film-air interface; C) EA/MAA copolymer only.